

INFORMATION REPORT

COUNTRY International  
SUBJECT Notes on Indium, Germanium, and Titanium

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- (a) A List of Indium Chemicals - dated 15 Jan 45
- (b) Extraction of Indium - dated 18 Jan 45
- (c) Purification of Indium - dated 18 Jan 45
- (d) Sources of Indium - dated 18 Jan 45
- (e) A List of Uses and Prospective Uses of Indium - undated
- (f) Sources of Germanium - dated 26 Jan 45
- (g) Uses and Alleged Possible Uses of Germanium - undated
- (h) Notes on Titanium - undated
- (i) Memorandum (Revised July 2, 1947) Metals, minerals, gases, and other substances which may have increased commercial interest owing to their association with the development of atomic energy.

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MEMORANDUM

1/18/45

Indium  
Extraction of Indium

Indium is usually extracted from indium-bearing ores, concentrates, minerals, metals, alloys, metallurgical residues, flue dust, calcines, fumes, distillation plant dust and other by-products by one of the following methods:

Method I. Zinc blends are dissolved in  $HNO_3$ , and the heavy metals are precipitated by  $H_2S$ . From the filtrate indium is precipitated with excess ammonia and this precipitation is repeated several times to remove zinc and manganese. The final  $In(OH)_3$  is dissolved in acetic acid and then precipitated as sulfide by  $H_2S$  as  $In_2S_3$ . To remove any remaining small amounts of iron, the  $In_2S_3$  is dissolved in  $HCl$ , a little  $HNO_3$  being added to oxidize the iron. Then the addition of  $NH_3$  precipitates  $Fe(OH)_3$  with only a little indium. After removing all the iron, pure  $In(OH)_3$  is precipitated by adding an excess of ammonia.

Method II. Indium-bearing zinc metal is treated with dilute  $H_2SO_4$  just insufficient to effect complete solution. A spongy mass of lead, copper, cadmium, tin, arsenic, iron and indium collects upon the residue of undissolved zinc. This spongy material is collected, washed, dissolved in  $HNO_3$ , and evaporated with  $H_2SO_4$ . The  $PbSO_4$  is filtered off, and the hydroxides of iron and indium are precipitated with  $NH_4OH$ . This precipitate is dissolved in a small amount of  $HCl$ , and the solution is brought close to the neutral point, then boiled with an excess of  $NaHSO_3$ . By this treatment a basic sulfite is obtained which has the formula  $In_2(SO_3).In_2(OH)_6.5H_2O$ . This is dissolved in  $H_2SO_4$ , and finally  $In(OH)_3$  is precipitated by an excess of  $NH_4OH$ .

Method III. A complex indium-bearing ore may be ground and then subjected to flotation by which concentrates of zinc and indium, lead, and silver are obtained. The zinc-indium concentrate may be treated as follows:

(A) Roasted with salt ( $NaCl$ ). The indium chloride is dissolved and metallic indium is deposited electrolytically.

(B) Dissolve in  $H_2SO_4$ , and precipitate the indium (a) by the addition of zinc, or (b) by neutralization of the excess acid.

The purity of the metal is increased by repeating the process. A purity of 99% and higher is claimed.

MEMORANDUM

1/18/45

Indium  
Purification of Indium

The most persistent impurity encountered in the isolation of indium is iron. The following methods have been suggested to effect the desired purification.

Method I. Precipitate  $\text{In}(\text{OH})_3$  from mixed solutions by adding  $\text{BaCO}_3$ .

Method II. Add  $\text{HCl}$ , evaporate to dryness, take up the residue with cold water, and treat with  $\text{H}_2\text{S}$ . Repeat the process several times.

Method III. Add  $\text{KCN}$  to mixed chlorides in acid solution, and extract  $\text{Fe}(\text{CNS})_3$  with ether.

Method IV. Add alcoholic pyridine solution to mixed chlorides, and precipitate  $\text{InCl}_3 \cdot 3\text{H}_2\text{O}$ . Both  $\text{FeCl}_3$  and  $\text{AlCl}_3$  remain in solution.

Method V. Sublime  $\text{InBr}_3$  in a stream of  $\text{CCl}_4$ , leaving  $\text{FeBr}_2$  as a residue.

MEMORANDUM

1/19/45

Indium  
Sources of Indium

Most of the available and reasonably recoverable indium is closely associated with zinc or zinc-bearing ores and minerals, and most of this indium is contained in the mineral sphalerite, either incorporated physically or in solid solution.

Hence it is obvious that most of the commercial indium is recovered as a by-product in some form of zinc metallurgy. It is safe to say, up to now, that no indium is recovered commercially as a result of the treatment of any indium-bearing material as a result of the treatment of such material for its indium content alone.

From an academic standpoint it is of interest to tabulate the various minerals known to contain indium, ranging from sphalerite, which contains relatively "substantial" quantities, down to those minerals wherein the metal occurs in minute or even infinitesimal percentages.

These minerals are:

1. Sphalerite, zinc sulfide,  $ZnS$ . In this mineral, the indium content usually ranges from 0.01% to 0.1%; rarely, if ever, in excess of 0.2%. As a matter of fact, the usual indium content of most sphalerite is, in all probability, less than 0.01%, or say less than 2 oz. per ton. Many samples of sphalerite give no indication of containing any indium as a result of ordinary chemical tests. For example, it is reported that the examination of 68 samples of zinc blende from various localities revealed the presence of indium in 37. On the other hand, it has been estimated that mid-western zinc concentrates may run as high as 10 oz. per ton.

2. A complex ore containing the sulfides of lead, zinc, iron, copper, silver and gold, owned by the Indium Corporation of America, near Kingman, Mohave County, Arizona, is reported to average 1.93 oz. of indium per ton. It is claimed that 50,000 tons of this ore has been developed, equivalent to 96,500 troy ounces of indium, or approximately one year's potential production of by-product indium at Anscoconda.

3. Zinc-bearing minerals other than sphalerite. The zinc content of these minerals is variable. It is probable that the indium content is roughly proportional to the zinc. The more abundant of these minerals, and hence those that are likely to contribute most of the available indium are indicated by an asterisk (\*) in the following alphabetical lists. The others, not so indicated, either contain minor percentages of zinc or they are relatively scarce or of local interest. It is almost certain that they are of little importance as sources of indium, but they are presented for the sake of completeness or for their academic interest.



- 2 -

1. **Alphacalcite**,  $2\text{ZnO} \cdot \text{CaO} \cdot \text{H}_2\text{O}$  or  $4\text{ZnO} \cdot \text{Ca}_2\text{O}_5 \cdot \text{H}_2\text{O}$   
 2. **Alphacalcite**,  $\text{ZnO} \cdot \text{P}_2\text{O}_5 \cdot 4\text{H}_2\text{O}$  (index of ref. 1.591)  
 3. **Alumite**,  $\text{Al}_2(\text{OH})_2(\text{SO}_4)_2$   
 4. **Arakawaite**,  $2\text{CuO} \cdot 2\text{ZnO} \cdot \text{P}_2\text{O}_5 \cdot 6\text{H}_2\text{O}$   
 5. **Auricalcite**,  $2(\text{Zn}, \text{Cu})\text{CO}_3 \cdot 3(\text{Zn}, \text{Cu})(\text{OH})_2$   
 6. **Austinite**,  $\text{CaMn}(\text{OH})\text{AsO}_4$   
 7. **Beryllitavandaniite**,  $2(\text{Mg}, \text{Mn}, \text{Zn})\text{O} \cdot 6\text{CaO} \cdot 4\text{BeO} \cdot \text{Al}_2\text{O}_3 \cdot 6\text{SiO}_3$   
 8. **Bethamphite**,  $3\text{ZnO} \cdot \text{P}_2\text{O}_5 \cdot 4\text{H}_2\text{O}$  (index of ref. 1.582)  
 9. **Brackebuschite**,  $(\text{Pb}, \text{Fe}, \text{Mn}, \text{Zn})_3 \cdot \text{V}_2\text{O}_5 \cdot \text{H}_2\text{O}$   
 10. **Brickerite**,  $4\text{ZnO} \cdot 3\text{CaO} \cdot 2\text{As}_2\text{O}_5$   
 11. **Calamine (hemimorphite)**,  $\text{H}_2\text{Zn}_2\text{SiO}_5$  or  $(\text{Zn OH})_2 \cdot \text{SiO}_3$  or  $\text{Zn}_4\text{SiO}_7(\text{OH})_2 \cdot \text{H}_2\text{O}$   
 12. **Chalcophanite**,  $(\text{Mn}, \text{Zn})\text{O} \cdot 2\text{MnO}_2 \cdot 2\text{H}_2\text{O}$   
 13. **Chlorophoenicite**,  $10(\text{Mn}, \text{Zn})\text{O} \cdot \text{As}_2\text{O}_5 \cdot 7\text{H}_2\text{O}$   
 14. **Clinohedrite**,  $\text{ZnO} \cdot \text{CaO} \cdot \text{SiO}_2 \cdot \text{H}_2\text{O}$   
 15. **Danalite**,  $3(\text{Fe}, \text{Zn}, \text{Mn})\text{O} \cdot 3\text{BeO} \cdot 3\text{SiO}_2$  or  $(\text{Fe}, \text{Zn})\text{S}$  or  $(\text{Fe}, \text{Fe}, \text{Zn}, \text{Mn})_7\text{Si}_3\text{O}_{12}\text{S}$  or  $(\text{Fe}, \text{Zn}, \text{Mn})_2(\text{Zn}, \text{Fe})_2\text{S} \cdot \text{Be}_3(\text{SiO}_4)_3$   
 16. **Deschloisite**,  $(\text{Pb}, \text{Zn})(\text{Pt}, \text{Zn})(\text{OH})_2$  or  $4(\text{Pb}, \text{Zn})\text{O} \cdot \text{V}_2\text{O}_5 \cdot \text{H}_2\text{O}$   
 17. **Dyalite**,  $(\text{Zn}, \text{Fe}, \text{Mn})\text{O} \cdot (\text{Al}, \text{Fe})_2\text{O}_3$   
 18. **Franklinite**,  $(\text{Fe}, \text{Zn}, \text{Mn})(\text{Fe}, \text{Mn})_2\text{O}_4$   
 19. **Gagerite**,  $8(\text{Mg}, \text{Mn}, \text{Zn})\text{O} \cdot 3\text{SiO}_2 \cdot 2\text{H}_2\text{O}$   
 20. **Gahnite**,  $\text{ZnAl}_2\text{O}_4$  or  $\text{ZnO} \cdot \text{Al}_2\text{O}_3$   
 21. **Glancocerinite**,  $10(\text{Zn}, \text{Cu})\text{O} \cdot 2\text{Al}_2\text{O}_3 \cdot 5\text{O}_2 \cdot 7\text{H}_2\text{O}$   
 22. **Goslarite**,  $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$  or  $\text{ZnO} \cdot \text{SO}_3 \cdot 7\text{H}_2\text{O}$   
 23. **Guadalupeite**,  $(\text{Hg}, \text{Zn})\text{S}$   
 24. **Heulandite**, (arsenic-bearing sphalerite)  
 25. **Herdystonite**,  $\text{Ca}_2\text{ZnSi}_2\text{O}_7$  or  $2\text{CaO} \cdot \text{ZnO} \cdot 2\text{SiO}_2$   
 26. **Hibbrite**,  $(\text{Mn}, \text{Fe})_2(\text{Mn}_2\text{S})\text{Be}_3(\text{SiO}_4)_3$   
 27. **Hemimorphite** (V. Calamine)  
 28. **Heterophyllite**,  $2\text{ZnO} \cdot 2\text{Mn}_2\text{O}_3 \cdot \text{H}_2\text{O}$  (index of ref. 2.344)  
 29. **Abnokitsonite**,  $22\text{ZnO} \cdot \text{MnO} \cdot 2\text{SiO}_2 \cdot \text{H}_2\text{O}$   
 30. **Holdenite**,  $2\text{ZnO} \cdot 4\text{ZnO} \cdot \text{As}_2\text{O}_5 \cdot 5\text{H}_2\text{O}$   
 31. **Hopite**,  $2\text{S}(\text{PO}_4)_2 \cdot \text{H}_2\text{O}$   
 32. **Hydrohlaerolite**,  $22\text{ZnO} \cdot 2\text{Mn}_2\text{O}_3 \cdot \text{H}_2\text{O}$  (V. heterophyllite)  
 33. **Hydrozincite**,  $22\text{ZnO} \cdot 3\text{Zn}(\text{OH})_2$  or  $\text{ZnCO}_3 \cdot 22\text{Zn}(\text{OH})_2$  or  $3\text{ZnO} \cdot \text{CO}_2 \cdot 2\text{H}_2\text{O}$   
 34. **Jeffersonite**,  $(\text{Mn}, \text{Zn}, \text{Fe}, \text{Mg})\text{O} \cdot \text{CaO} \cdot 2\text{SiO}_2$   
 35. **Koettigite**,  $\text{ZnO} \cdot \text{As}_2\text{O}_5 \cdot 8\text{H}_2\text{O}$  or  $\text{Zn}_3\text{As}_2\text{O}_8 \cdot 8\text{H}_2\text{O}$   
 36. **Kreittonnite**,  $(\text{Zn}, \text{Fe}, \text{Mg})\text{O} \cdot (\text{Al}, \text{Fe})_2\text{O}_3$   
 37. **Larsenite**,  $\text{PbZnSiO}_4$  or  $\text{PbO} \cdot \text{ZnO} \cdot \text{SiO}_2$   
 38. **Legrandite**,  $26 \text{ZnO} \cdot 9\text{As}_2\text{O}_5 \cdot 25\text{H}_2\text{O}$   
 39. **Leucophoenicite**,  $8(\text{Mn}, \text{Zn}, \text{Ca})\text{O} \cdot 3\text{SiO}_2 \cdot \text{H}_2\text{O}$   
 40. **Lossyite**,  $7(\text{Mn}, \text{Zn}, \text{Mg})\text{O} \cdot 2\text{CO}_2 \cdot 5\text{H}_2\text{O}$   
 41. **Manganotantalite**,  $\text{MnO}(\text{Ta}, \text{Cb})_2\text{O}_5$   
 42. **McGovernite**,  $21(\text{Mn}, \text{Mg}, \text{Zn})\text{O} \cdot 3\text{SiO}_2 \cdot 2\text{As}_2\text{O}_3 \cdot \text{As}_2\text{O}_5$   
 43. **Macreite**,  $4(\text{Mg}, \text{Mn}, \text{Zn})\text{O} \cdot \text{SO}_3 \cdot 11\text{H}_2\text{O}$   
 44. **Nicholsonite** (a zinc-bearing aragonite with zinc up to 10%, found in Nevada)  
 45. **Nicholsonite**; theoretical formula possibly:  $5\text{ZnCO}_3 \cdot 21\text{CaCO}_3$   
 46. **Paraurthalcite** (a zinc-malachite)(?)  
 47. **Phosphophyllite**,  $3(\text{Zn}, \text{Fe}, \text{Mn})\text{O} \cdot \text{P}_2\text{O}_5 \cdot 4\text{H}_2\text{O}$   
 48. **Pittsacite**,  $(\text{Pb}, \text{Cu}, \text{Zn})_3 \cdot \text{V}_2\text{O}_5 \cdot (\text{Pb}, \text{Cu}, \text{Zn})(\text{OH})_2 \cdot \text{H}_2\text{O}$  or  $4(\text{Pb}, \text{Cu}, \text{Zn})\text{O} \cdot \text{V}_2\text{O}_5 \cdot \text{H}_2\text{O}$

Calcite,  $\text{CaCO}_3$   
 Siderite,  $\text{FeCO}_3$   
 Spinel,  $\text{Mg, Mn, ZnO} \cdot (\text{Al, Fe, Mn})_2\text{O}_3$   
 Buserite,  $(\text{Mn, Mg, Zn})\text{BO}_2$   
 Turquoise,  $\text{Cu, P, O}_5 \cdot \text{Zn}(\text{OH})_2$   
 Tennantite,  $(\text{Cu, Fe, Zn, Ag})_{12}\text{As}_4\text{S}_{13}$  or generally  $\text{Cu}_8\text{Fe}_2\text{S}_8$  or  $\text{Cu}_6\text{Fe}_2\text{S}_8$   
 Brookite,  $(\text{Mn, Mn})_2\text{SiO}_4$  (another name for Willemite,  $\text{Zn}_2\text{SiO}_4$  or  $2\text{ZnO} \cdot \text{SiO}_2$ )  
 Veselyite,  $7(\text{Cu, Zn}) \cdot 8(\text{OH}) \cdot (\text{P, As})_2\text{O}_5 \cdot 9\text{H}_2\text{O}$  or  $7(\text{Mn, Zn}) \cdot (\text{P, As})_2\text{O}_5 \cdot 9\text{H}_2\text{O}$   
 Voltsite,  $2\text{ZnS} \cdot \text{ZnO}$  or  $\text{Zn}_3\text{S}_4$   
 Willemite,  $\text{Zn}_2\text{SiO}_4$  or  $2\text{ZnO} \cdot \text{SiO}_2$   
 Wolfstonite (a magnetic oxide of manganese and zinc, containing about 47% Mn and 19% Zn, and a trace of Fe; theoretical formula possibly  $16\text{MnO}_2 \cdot 15\text{ZnO} \cdot x\text{FeO}$ )  
 Turquoise,  $\text{ZnS}$   
 Yentramite,  $(\text{Mn, Zn})_{16}\text{Sb}_2\text{Si}_2\text{O}_{20}$   
 Zincaluminite,  $22\text{ZnSO}_4 \cdot 4\text{Zn}(\text{OH})_2 \cdot 6\text{Al}(\text{OH})_3 \cdot 5\text{H}_2\text{O}$  or  $62\text{ZnO} \cdot 3\text{Al}_2\text{O}_3 \cdot 28\text{SO}_3 \cdot 18\text{H}_2\text{O}$   
 Zinc-Copper Melanterite,  $\text{CuO} \cdot \text{ZnO} \cdot 2\text{SO}_3 \cdot 14\text{H}_2\text{O}$   
 Zincite,  $\text{ZnO}$   
 Zimshofferite,  $(\text{Mg, Mn, Zn})\text{O} \cdot \text{CaO} \cdot 2\text{SiO}_2$   
 Zinkite,  $\text{ZnSCl}_2 \cdot 7\text{H}_2\text{O}$

4. Minerals which do not contain Zinc but which frequently contain Indium:

- \*Astrophyllite,  $(\text{Na}, \text{K})_4(\text{Fe}, \text{Mn})_4\text{Ti}(\text{SiO}_4)_4$
- \*Cassiterite,  $\text{SnO}_2$
- \*Copper Ores (such as tennantite and tetrahedrite)
- \*Ruebnerite,  $\text{MnWO}_4$
- \*Iron Ores (such as pyrite and pyrrhotite)
- \*Lead Ores (such as galena, cerussite and anglesite)
- \*Manganotantalite,  $\text{MnO}(\text{Ta}, \text{Cb})_2\text{O}_5$
- \*Pegmatites (usually consist of microcline or orthoclase, quartz and muscovite)
- \*Phlegopite,  $\text{KMg}_3\text{Al}_2\text{Si}_3\text{O}_{10}(\text{OH})_2$  or  $2\text{K}_2\text{O} \cdot 10(\text{Mg}, \text{Fe})\text{O} \cdot 3\text{Al}_2\text{O}_3 \cdot 12\text{SiO}_2 \cdot 2\text{H}_2\text{O}$  or  $(\text{H}, \text{K}(\text{Mg}, \text{F}))_3\text{Mg}_3\text{Al}(\text{SiO}_4)_3$  or  $\text{H}_2\text{KMg}_3\text{Al}(\text{SiO}_4)_3 + \text{K}(\text{Mg}, \text{F})\text{Mg}_2\text{Al}(\text{SiO}_4)_3$
- \*Pyrite,  $\text{FeS}_2$
- \*Pyrrhotite,  $\text{Fe}_x\text{S}$  or  $\text{Fe}_x\text{S}_y$  or  $\text{Fe}_{11}\text{S}_{12}$ , actually varies from  $\text{Fe}_5\text{S}_6$  to  $\text{Fe}_{10}\text{S}_{11}$
- \*Rhodonite,  $\text{MnSiO}_3$
- \*Samarakite,  $(\text{Fe}, \text{Ca}, \text{UO}_2)_3(\text{Ce}, \text{Yttr}, \text{TaO}_2, \text{ZrO}_2)_3(\text{Nb}, \text{Ta})_6\text{O}_{21}$ . This mineral is essentially a columbate (niobate) and tantalate of iron and calcium with the cerium(Ce) and yttrium(Yttr) metals, together with uranium oxide. The yttrium oxides vary from 6 to 15%, and the cerium oxides from 2 to 6%. Tantalum pentoxide,  $\text{Ta}_2\text{O}_5$ , and columbium pentoxide,  $\text{Cb}_2\text{O}_5$  (same as niobium pentoxide,  $\text{Nb}_2\text{O}_5$ ) make up about 50%. The formula is sometimes written  $3(\text{Fe}, \text{Ca}, \text{UO}_2)\text{O} \cdot (\text{Ce}, \text{Y})_2\text{O}_3(\text{Cb}, \text{Ta})_2\text{O}_5$  or  $(\text{Fe}, \text{Ca}, \text{UO}_2)_3(\text{Ce}, \text{Y})_2(\text{Nb}, \text{Ta})_6\text{O}_2$
- \*Siderite,  $\text{FeCO}_3$
- \*Wolframite,  $(\text{Fe}, \text{Mn})\text{WO}_4$
- \*Zircon,  $\text{ZrSiO}_4$

5. Metals, Alloys and Metal Salts which frequently contain Indium, or with which it is closely associated:

- Cadmium, Cd  
Cobalt, Co  
Gallium, Ga

-4-

Iron Sulfide,  $\text{FeS}$ ,  $\text{FeS}_2$ , and  $\text{Fe}_2\text{S}_3$   
Lead Sulfide,  $\text{PbS}$   
Thallium,  $\text{Tl}$   
Zinc Sulfide,  $\text{ZnS}$

6. Residues and By-Products at smelters and other Metallurgical and Chemical Manufacturing plants, such as:

Bag-house fume  
Blue powder from distillation of zinc ores  
Brass furnace flue dust  
Cadmium-bearing flue dust  
Cadmium sponge (0.14 to 0.2 oz. per ton)  
Calcines  
Chloride fume (0.25 to 0.3 oz. per ton)  
Chloridized calcines (0.3 to 0.5 oz. per ton)  
Cobalt cake (4 to 5 oz. per ton)  
Condensed flue dust and fume from brass-casting furnaces.  
Copper blast-furnace fume  
Copper cake (0.02 to 0.05 oz. per ton)  
Cottrell plant fume  
Distillation plant dust and fume  
Electrolytic plant dust and fume  
Filtration plant sludges and residues  
Flue dust (from roasting and remelting furnaces, and sintering machines)  
Fumes (from roasting furnaces and sintering machines)  
Furnace fumes  
Lead blast-furnace fume  
Lithopone plant by-products and residues  
Metallurgical residues  
Refinery residues (electrolytic zinc)  
Residues from electrolytic lead refineries  
Roasting-furnace fume  
Shriver cake (0.04 to 0.05 oz. per ton)  
Sintering machine dust and fume  
Smelter by-products  
Vat residues from electrolytic zinc plants  
Vat residues from zinc liquors in the manufacture of lithopone  
Zinc dust formed in the distillation of zinc ores  
Zinc residues (0.25 to 0.5 oz. per ton)



A List of Uses and Prospective Uses of Indium

Age-hardening of aluminum alloys  
Age-hardening of copper alloys  
Aircraft instrument protection against damage by salt water spray  
Airplane engine bearings  
Airplane propellers  
Alloy age-hardening  
Alloying ingredient for silver  
Alloys  
Aluminum alloy age-hardening  
Amalgams (dental)  
Automobile hardware  
Babbitts  
Ball bearings  
Band instruments  
Barber chair and equipment trim  
Bearings  
Bearing surfaces  
Brass band instruments  
Brasing alloys  
Bus engines  
Cadmium conservation  
Cadmium-indium alloys  
Cadmium-silver bearings (plating of)  
Cartridge cases  
Castings (dental)  
Cast silver  
Ceramics  
Checking oxidation  
Chemicals (best known are: trichloride,  $\text{InCl}_3$ ; sulphate,  $\text{In}_2(\text{SO}_4)_3 \cdot 5\text{H}_2\text{O}$ ; and sesquioxide,  $\text{In}_2\text{O}_3$ )  
Clips  
Close-tolerance plating  
Coating for silver  
Colorant in glass (yellow)  
Combat aircraft engine bearings  
Compounds  
Compressive strength in dental alloys  
Conservation of other metals  
Contact points (electrical)  
Control rods (Ordinance)  
Copper alloy age-hardening  
Copper-indium alloys  
Copper-lead bearings  
Corrosion resistant  
Cylinder wall protection  
Dairy equipment coatings  
Decorative finishes

Dental alloys  
 Dental chair and equipment trim  
 Dental instrument plating  
 Diesel engines  
 Diesel marine engines  
 Die-stuff mordant  
 Diffused plating  
 Diffusion coatings  
 Electrical contacts  
 Engine bearings  
 Experimental work at Watervliet Arsenal  
 Fatigue prevention  
 Finishes (decorative)  
 Finishing metal surfaces  
 Flash coatings on cadmium, silverware, and dental equipment.  
 Floodlights (reflecting surfaces)  
 Flow-under-pressure resistance  
 Formability increases  
 Fusible alloys  
 Glass colorant (yellow, any shade from light canary to tangerine)  
 Glass manufacture  
 Gun carriages (plating)  
 Gun leveling plates  
 Hardening metals (age-hardening of Cu and Al)  
 Hardness increases in metals  
 Hardware (exterior trim)  
 Hardware for automobiles  
 Headlights (plating)  
 Headlights (reflectors)  
 High-duty internal combustion engines  
 High-polish surfaces  
 High-temperature thermometers  
 Reproduction of metal surfaces  
 Indium-cyanide-dextrose plating bath.  
 Indium plating  
 Indium-treated lead (stronger and harder)  
 Rings in spectacle frames  
 Instruments (medical)  
 Instrument protection  
 Jewelry (Plating and alloys)  
 Leveling plates for guns  
 Light reflectors  
 Low-melting alloys  
 Lubrication (Machine-gun parts)  
 Machine gun parts  
 Machine tools (plating)  
 Mirror finished deposits  
 Molting range increases in alloys  
 Mordant alloys (anodizing)  
 Metal age-hardening  
 Metal finishing

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Military uses  
Mirrors (front-surfaced)  
Mordant for die stuffs  
Motor car trim  
Musical instruments  
Nickel-indium alloys  
Non-corrosive coatings  
Non-ferrous metal plating  
Optical glass  
Optical goods (plating)  
Ordnance  
Oxidation resistant  
Pharmaceuticals  
Pin hole smearing  
Piston protection  
Plating parts for machine guns  
Plungers (ordnance)  
Polished fixtures  
Propellers (airplanes)  
Protection of metals against organic acids in lubricants  
Protection of metals against salt-water spray  
Pratt & Whitney engines  
Reflectors (plating)  
Research  
Resistance to tarnish  
Rifle Clips  
Rolls-Royce aircraft engine bearings  
Salt spray protection  
Searchlights (reflectors)  
Setting-change resistance  
Shoulder bushings (ordnance)  
Silver alloy ingredient  
Silver-indium bearings  
Silverware  
Small arms bearings  
Small pins (in hinges of spectacles)  
Smearing to close pin holes  
Solders (increases fusibility and wetting qualities)  
Soluble anodes  
Spectacle frame hinges  
Stability increase of metals  
Steel-backed bearings  
Steel blade propellers  
Steel protection (after a flash coating of another metal)  
Steel rods (plating)  
Strength increase of dental alloys (compressive)  
Surface diffusion  
Surface hardness  
Surgical instruments plating  
Synthetic anti-malarials

MEMORANDUM

January 26, 1944

Germanium  
Sources of Germanium

Germanium is widely distributed in nature, but it occurs usually in minerals which are very rare or in more abundant minerals in minute quantities. It is usually found as a sulfide or associated with sulfide ores. The minerals wherein it is found are divided into two classes, namely those known to contain germanium as a compound, and having been so identified mineralogically, and those wherein it is held mechanically, or possibly in solid solution.

1. Minerals wherein germanium occurs as a constituent are listed as follows:

Argyrodite,  $\text{Ag}_2\text{GeS}_3$  or  $3\text{Ag}_{20}\text{GeS}_{17}$ , or  $4\text{Ag}_{20}\text{GeS}_{17}$ , containing from 1% to 7% germanium. Winkler first isolated the metal from this mineral, the sample coming from Freiberg, Germany. It is found also in the silver mines of Ormo, Bolivia.

Canfieldite,  $4\text{Ag}_2\text{S}(\text{Sn},\text{Ge})\text{S}_2$ , containing from 1.32% to 6.5% germanium. Also found in Bolivia.

Kuxenite, a complex mineral containing Pt, Ti, Zr, Ce, U, and Th. It is a recognized source of Ge, Zr, and Nb. Its probable formula is  $\text{Pt}_2\text{Ti}_2\text{Zr}_2\text{Ce}_2\text{U}_2\text{Th}_2\text{Fe}(\text{Ge})_2$ .

Germanite,  $\text{Cu}_2\text{Ge}(\text{Ge})_2$  or  $5\text{Cu}_2\text{Ge}(\text{Ge})_2\text{As}_2\text{S}_3\text{ZnGeS}_2$ . This mineral is found in South West Africa. Its germanium content varies from 1% to 8.7%. Following are analyses of two different lots of a native ore of this type:

Lot I		Lot II	
Cu	44.01%	Cu	38.60%
S	30.96	S	26.90
Fe	5.08	Fe	4.20
As	6.83	As	7.36
Zn	2.74	Zn	4.00
Pb	2.26	Pb	7.90
Ga	0.57	Ga	0.14
Ge	1.00	Ge	3.08
Mo	0.03	Mo	0.28
$\text{SiO}_2$	1.84	Balance	7.94
$\text{BaSO}_4$	0.02		100.00%
17 other elements	0.66		
Total	100.00%		

Ultrabesite,  $28\text{PbS} \cdot 11\text{Ag}_2\text{S} \cdot 3\text{GeS}_2 \cdot 25\text{Sb}_2\text{S}_3$ . This is a sulfide ore of lead, silver and antimony, containing about 2.2% germanium. It is found in Freiberg, Saxony.

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2. Sphalerites constitute the most abundant source of germanium. It appears that the low-temperature deposits contain a higher percentage of germanium than the high-temperature deposits. Sphalerite from Joplin, Mo. and Picher, Okla. carry as much as 0.1% to 1.0% gallium, and the metal is found in the zinc blendes of Butte, Mont. Wisconsin ores are reported to carry 0.01% gallium. Certain British blendes are said to contain 2% to 4%.

Urban made a spectroscopic examination of 64 specimens of zinc blendes from widely scattered areas and found germanium in 38 of them. Similarly, the spectroscopic examination of 68 Spanish zinc blendes revealed gallium in 50 specimens.

Its recovery as a by-product in zinc metallurgy is simple since the metal either burns to  $\text{GeO}_2$  and collects in the bag-house dust or Cottrell dust; or the oxide is reduced by carbon at a red heat, and since the metal is only slightly volatile at  $1350^\circ \text{C.}$ , it collects in the spelter retort residues.

3. Other minerals wherein Germanium has been found:

Bauxite, a mixture of aluminum or aluminum hydroxides, varying from  $\text{Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$  to  $\text{Al}_2\text{O}_3 \cdot 2\text{H}_2\text{O}$  and  $\text{Al}_2\text{O}_3 \cdot \text{H}_2\text{O}$ , usually  $\text{Al}_2\text{O}_3 \cdot 2\text{H}_2\text{O}$

Cassiterite,  $\text{SnO}_2$

Columbite,  $(\text{Fe}, \text{Mn})(\text{Cb}, \text{Ta})_2\text{O}_6$

Copper (native copper), Cu

Erargite,  $3\text{Cu}_2\text{S} \cdot \text{As}_2\text{S}_5$  (usually from a trace to .01%; in Butte, Mont. sometimes as high as 0.1%  $\text{GeO}_2$ )

Feldspars, silicates of Al with K, Na, and Ca, rarely Ba.

Frankelite,  $\text{Pb}_5\text{FeSn}_3\text{Sb}_2\text{S}_{14}$  (a rare tin-lead sulfostibide)

Graphite, C

Lepidolite,  $(\text{K}, \text{Li})_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 3\text{SiO}_2 \cdot \text{F}$  or  $\text{K}_2\text{Li}_3\text{Al}_4\text{Si}_7\text{O}_{21}(\text{OH}, \text{F})_3$

Leucite,  $\text{K}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 4\text{SiO}_2$  or  $\text{KAlSi}_2\text{O}_6$

Meteorites, (found in seven types)

Mica; especially lepidolite, but also in biotite,  $(\text{K}, \text{Mg})_2\text{O} \cdot 2(\text{Al}, \text{Fe})_2\text{O}_3 \cdot 3\text{SiO}_2$ , and muscovite,  $\text{K}_2\text{O} \cdot 3\text{Al}_2\text{O}_3 \cdot 6\text{SiO}_2$

Pegmatite dykes (usually in the silicate constituents)



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Samaraskite,  $(\text{Fe}, \text{Ca}, \text{UO}_2)_3(\text{Ce}, \text{Yttr}, \text{TnO}_2, \text{ZrO}_2)_3(\text{Nb}, \text{Ta})_6\text{O}_{21}$ . This mineral is essentially a columbate (niobate) and tantalate of iron and calcium with the cerium (Cer) and yttrium (Yttr) metals, together with uranium oxide. The yttrium oxides vary from 6 to 15%, and the cerium oxides from 2 to 6%. Tantalum pentoxide,  $\text{Ta}_2\text{O}_5$ , and columbium pentoxide,  $\text{Cb}_2\text{O}_5$  (same as neobium pentoxide,  $\text{Nb}_2\text{O}_5$ ) make up about 56%. The formula is sometimes written  $3(\text{Fe}, \text{Ca}, \text{UO}_2)_3(\text{Ce}, \text{Y})_2(\text{Cb}, \text{Ta})_2\text{O}_5$  or  $(\text{Fe}, \text{Ca}, \text{UO}_2)_3(\text{Ce}, \text{Y})_2(\text{Nb}, \text{Ta})_6\text{O}_{21}$ .

Silicates, from pegmatite dykes

Smithsonite,  $\text{ZnCO}_3$ , near Salem, Ky., assays as high as 0.01%  $\text{GeO}_2$

Spodumene,  $\text{LiAlSi}_2\text{O}_6$

Tantalite,  $(\text{Fe}, \text{Mn})\text{Ta}_2\text{O}_6$

Tin Ores (found in 8 out of 12)

Topaz,  $\text{Al}_2\text{O}_3(\text{OH}, \text{F})\text{SiO}_2$ . Germanium usually present. It was found in each of 34 specimens. A topaz from Silver Leaf Mine, Manitoba, assayed 0.1%  $\text{GeO}_2$ .

Tourmaline, a borosilicate of K, Li, Mg, Fe, and Al. Formula uncertain. It may be:  $(\text{Na}, \text{Ca})(\text{Al}, \text{Fe}, \text{Li}, \text{Mg})_3\text{B}_3\text{Al}_3(\text{AlSi}_2\text{O}_9)_3(\text{O}, \text{OH}, \text{F})_4$

#### 4. Other Materials and By-products which are sources of Germanium.

Bag-house dust

Cadmium electrolyte

Coal (near Newcastle, England and in certain U. S. low-ash coals)

Cottrell dust

Dust (bag-house, Cottrell, and flue dust)

English coal, near Newcastle, carries as much as 1.6%  $\text{GeO}_2$

Flue dust

Gas works dust (0.15% to 1.4%  $\text{GeO}_2$ )

Low-ash coals in U. S.

Mineral waters

Newcastle coal (England)

Residues recovered in the production of spelter.

Sea plants

Soils (sometimes 0.005% Ga. said to stimulate plant growth)

Solar spectrum (scientific interest)

Spelter retort residues.

Zinc oxide from flue dust.

Syrup cups (plating)  
Turnish resistant  
Temperature control apparatus  
Thermometers (high-temperature)  
Tin-indium alloys  
Tin-lead solders  
Tools (plating)  
Trin (external hardware)  
Trin for automobiles  
Trunk engines  
Typewriter assemblies  
Washers (plating)  
Wearing quality of bearings increased  
Wear-resistance coatings  
White Motor bearings  
Wire  
Zinc-indium alloys  
Zinc-indium coatings on propellers

# Uses and Possible Uses of Germanium

Absorption spectra of glass were widely dispersed  
 Anticorrosive coatings produced with silica glass  
 Birmah engine alloys (strength and light wt.)  
 Aluminum-germanium alloys  
 Alloys with mercury, aluminum, magnesium, silver and copper  
 Anemia remedy  
 Cancer lesions  
 Corrosion treatment proposed  
 Chemicals  
 Constituent of optical glass  
 Copper-Ge alloys  
 Corrosion-resistant alloys  
 Density of hard-crown glass increased  
 Dental inlays (Ge-Au alloys)  
 Devitrification of glass increased  
 Dispersion quality of glass increased  
 Displaces silver from its solutions  
 Durability of glass decreased  
 Expansion coefficient of glass increased slightly  
 Experimental work  
 Fatigue-reducing alloys  
 Germanium-aluminum alloys  
 Gold-Ge alloys  
 Hardness of magnesium and copper increased  
 Magnesium-Ge alloys  
 Mercury-Ge alloys  
 Optical glass refractive power increased  
 Pernicious anemia remedy  
 Pharmaceutical in treatment of pernicious anemia  
 Refractive index of flint glass increased  
 Research  
 Rolling qualities of aluminum said to be improved (?)  
 Silver-Ge alloys  
 Softening temperature of glass lowered  
 Strength of aluminum said to be increased (?)

## NOTES ON TITANIUM

### SUMMARY

(A brief topical condensation of over 1000 references and reports)

#### I. HISTORY.

1. Discovery by Rev. William Gregor in 1789, in Ilmenite.
2. Found by Klaproth in 1795, in Rutile.
3. Pure oxide prepared by Rose in 1821.
4. Pure metal prepared by Hunter in 1910.

#### II. OCCURRENCE IN NATURE.

1. Eighth most abundant metal, and ninth most abundant element, constituting 0.61% of the earth's crust.
2. Geographical distribution.
3. Rocks.
4. Minerals.
5. Ores.
6. Associations.

#### III. OCCURRENCE OF A BY-PRODUCT in the treatment or recovery of other metals or mineral substances.

#### IV. PHYSICAL PROPERTIES.

1. Atomic weight 47.88.
2. Atomic number 22.
3. Isotopes 46, 47, 48, 49, 50.
4. Melting point 1660°C.
5. Boiling point above 3000°C.
6. Density 4.5.
7. Electrical resistivity  $3 \times 10^{-6}$  ohm-cm.
8. Radius  $M^{+4}$  ion in crystals  $1.84 \text{ cm.} \times 10^{-8}$ .
9. Ductility, hardness, luster, etc.

#### V. CHEMICAL PROPERTIES.

1. Chemical reactions.
2. Affinities.
3. Heats of formation.
4. Stability.
5. Unique characteristics, etc.

#### VI. DETECTION.

Twelve qualitative methods.

#### VII. ESTIMATION.

1. Gravimetric methods.
2. Volumetric methods.
3. Colorimetric methods.
4. Oxidimetric methods.
5. Analysis of titanium materials.
6. Preparation of reagents.

theory.  
 2. Applications of chemical theory.

#### III. TITANIUM.

1. Present state of development.  
 2. Basic methods of preparing elemental titanium.  
 3. Form of product.

#### IV. TITANIUM.

1. Four basic classes and their variations.  
 2. Individual compounds and their characteristics.  
 3. Perfluorinated compounds.

#### V. USES.

1. Uses of elemental titanium.
2. Alloys.
3. Refractories: grades, uses and beneficial effects.
4. Applications and functions in steel.
5. Applications in cast iron.
6. Effects on magnetic properties, grain size, etc.
7. Incandescent media for lighting purposes.
8. Dyes, mordants, bleaching agents, strippers, etc.
9. Refractory materials and ceramics, glasses, enamels, glazes, and bricks.
10. Salts as reducing agents.
11. Smoke screens and pyrotechnics.
12. Woods.
13. Coagulants.
14. Pigments and their preparation and properties.
15. Effects of refractive indices.
16. Paper.
17. Nylon.
18. Rubber.
19. Linoleum.
20. Leather.
21. Plastics.
22. Abrasives.
23. Catalysts.
24. Printing ink.
25. Silk printing.
26. Welding rods.
27. Tooth paste.
28. Face powders.
29. Gels.
30. Medicinal preparations.
31. Nitrogen fixation.
32. Phosphorus pentoxide liberation.
33. Applications in pure science.
34. Numerous special applications.

#### VI. COST.

#### VII. SOURCES AND PRICES.



MEMORANDUM  
(Revised July 2, 1947)

Metals, minerals, gases, and other substances which may have increased commercial interest owing to their association with the development of atomic energy.

Note: Not strictly confidential, but not for general circulation.

\* These items are of special importance.

Actinium (radioactive)  
\*Aluminum (for cooling pipes)  
Barium  
Antimony  
\*Beryllium (for cooling pipes)  
\*Bismuth (molten, for cooling; solid, for cooling pipes)  
Boron  
Bromine  
\*Cadmium (absorber)  
\*Carbon (moderator)  
Chemicals (in uranium chemistry)  
Chlorine  
\*Concrete (shielding)  
Corrosion-resistant alloys  
Detector materials (rhodium, indium, iodine)  
Deuterium (heavy hydrogen)  
Dysprosium (absorber)  
Europium (absorber)  
Fluorine  
\*Fluorite  
Gadolinium (absorber)  
\*Gallium (in alloys; and in atomic research)  
Germanium (in alloys; and in atomic research)  
\*Graphite (moderator; and in "pile" construction)  
\*Heavy water (moderator)  
Helium (for cooling)  
Hydrogen  
Indium (detector; and as foil)  
Iodine (detector)  
Lanthanum  
\*Lead (for cooling pipes; and for shielding)  
Lithium  
\*Magnesium (for cooling pipes)  
Mercury  
Metal foils  
Moderators (carbon, graphite, heavy water)  
\*Monazite (source of thorium)  
Nitrogen  
Oxygen  
Tellurium  
Paraffin  
Polonium

Protactinium (radioactive)  
Radium (radioactive)  
Radioactive minerals (~~see special list~~)  
Rhodium (detector)  
Selenium  
Samarium (absorber)  
•Steel (shielding)  
Tellurium  
•Tin (for cooling pipes)  
Thorium (radioactive)  
Titanium (alloys; refractories; atomic research)  
Tungsten  
•Uraninite (important mineral source)  
•Carnotite (important mineral source)  
•Uranium (chief source of fissionable material)  
Uranium-bearing minerals (~~see special list~~)  
Water (for cooling)  
•Zinc (for cooling pipes)  
Zirconium